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(54) Title of the Invention:

CONDUCTIVE POLYMER COMPOSITION

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SPECIFICATION1. Title of the Invention:**CONDUCTIVE POLYMER COMPOSITION**2. Scope of the Patent Claim(s):

1. A conductive polymer composition consisting of a liquid diene-based polymer that

contains one of hydroxyl groups, carboxyl groups, acryloyl groups, and methacryloyl groups, a radical generator, and a conductive material.

2. The composition described in Claim 1, wherein the liquid diene-based polymer is a liquid diene-based polymer that contains one of hydroxyl groups, carboxyl groups, acryloyl groups, and methacryloyl groups at the terminals of the molecule.

3. The composition as described in Claim 1, wherein the amount of the radical generator added is 0.1–30 parts by weight per 100 parts by weight of the liquid diene-based polymer.

4. The composition as described in Claim 1, wherein the radical generator is benzoyl peroxide or dicumyl peroxide.

5. The composition as described in Claim 1, wherein the conductive material is a material selected from among metal powder, metal fiber, metal oxides, metal-coated fiber, carbon powder, carbon fiber, and mixed conductive materials of metals or metal oxides and other conductive materials.

3. Detailed Description of the Invention

Area of Industrial Application

The present invention pertains to conductive polymer compositions and, in more detail, to conductive polymer compositions that can be produced with ease and moreover provide elastic cured materials having excellent conductivity.

Prior Art and Problems to be Solved by the Invention

Thus far, a form of conductive rubber is known that is prepared by adding conductive materials such as metals, metal oxides, or metal halides to natural rubber or synthetic rubber.

However, there have been various problems with producing this conductive rubber. In other words, it is difficult to add and disperse the conductive material uniformly in natural rubber or synthetic rubber at ordinary temperatures, because the rubber is solid at ordinary temperatures; thus, to add and disperse the conductive material uniformly, the rubber has to be heated to relatively high temperatures and then the mixture has to be intensively mix-kneaded by applying a high torque. Furthermore, the following method has been employed, depending on the type of conductive material used, to incorporate the conductive material, namely, placing the rubber in a sealed vessel, feeding the conductive material into the vessel under reduced pressure, and diffusing it. However, certain aspects of this process are inconvenient, such as the fact that special equipment is required, a complicated procedure is involved, and considerable time is required for the incorporation.

An Approach to Solving the Problems

The present inventor carried out extensive studies to solve the above-mentioned problems, and found that a liquid polymer composition that can be produced with ease, and moreover that provides an elastic cured material having excellent conductivity, can be obtained by using three ingredients, i.e., a specified liquid diene-based polymer, a radical generator, and a conductive material, in combination. It was this finding that led to the development of the present invention.

Specifically, the present invention provides a conductive polymer composition consisting of a liquid diene-based polymer having one of hydroxyl groups, carboxyl groups, acryloyl groups, and methacryloyl groups, a radical generator, and a conductive material.

The liquid diene-based polymer to be used in the present invention is a liquid diene-based

polymer having one of hydroxyl groups, carboxyl groups, acryloyl groups, and methacryloyl groups within the molecule or at the terminals of the molecule. Such liquid diene-based polymers include polymers and copolymers of dienes with 4-12 carbon atoms, and moreover copolymers of these diene monomers with α -olefinic addition-polymerizable monomers with 2-22 carbon atoms.

Liquid diene-based polymers with hydroxyl groups that can be used are usually those with number-average molecular weights of 300-25,000, and preferably 500-10,000, and hydroxyl group contents of 0.1-10 mEq/g, and preferably 0.3-7 mEq/g. Specific examples include butadiene homopolymers, isoprene homopolymers, butadiene-styrene copolymers, butadiene-isoprene copolymers, butadiene-acrylonitrile copolymers, butadiene-2-ethylhexylacrylate copolymers, and butadiene-*n*-octadecylacrylate copolymers. These liquid diene-based polymers with hydroxyl groups can be produced, for example, by reacting conjugated diene monomers in the presence of hydrogen peroxide in a liquid reaction medium with heating.

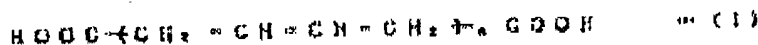
Examples of liquid diene-based polymers with carboxyl groups are those represented by the following formula (I), and those with carboxyl groups at the terminals of the molecule are preferred. Liquid diene-based polymers with carboxyl groups can be produced, for example, by reacting conjugated diene monomers with maleic anhydride, etc.

Examples of liquid diene-based polymers with acryloyl groups are those represented by the following formula (II), and those with acryloyl groups at the terminals of the molecule are preferred. Liquid diene-based polymers with acryloyl groups can be produced, for example, by reacting the aforementioned liquid diene-based polymers with hydroxyl groups with acrylic acid,

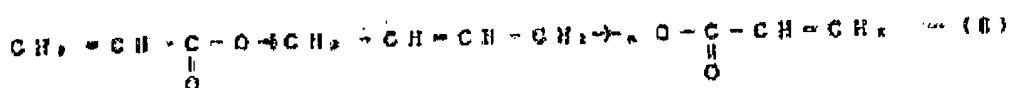
etc.

Examples of liquid diene-based polymers with methacryloyl groups are those represented by the following formula (III), and those with methacryloyl groups at the terminals of the molecule are preferred. Liquid diene-based polymers with methacryloyl groups can be produced, for example, by reacting the aforementioned liquid diene-based polymers with hydroxyl groups with methacrylic acid, etc.

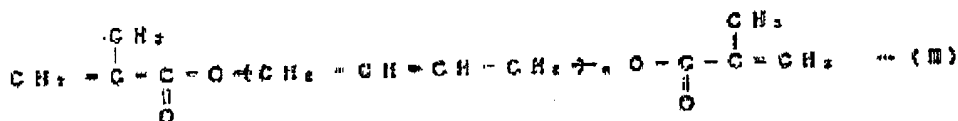
One of these liquid diene-based polymers with hydroxyl groups, carboxyl groups, acryloyl groups, or methacryloyl groups is usually used singly, but combinations of two or more can also be used.



(In the formula, n represents an integer of 4-500, and preferably 8-200.)



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The radical generator to be used in the present invention is not particularly critical, and can be selected randomly from among the known ones. Examples of those usually used include benzoin, benzoyl methyl ether, benzophenone, benzoyl peroxide, lauryl peroxide, dicumyl peroxide, methyl ethyl ketone peroxide, and azobisisobutyronitrile. The amount usually added is 0.1-30 parts by weight per 100 parts by weight of the aforesaid liquid diene-based polymer, and preferably 1-10 parts by weight. The addition of a radical generator to the aforesaid liquid

diene-based polymer brings about the formation of an effective three-dimensional structure.

The conductive material to be used in the present invention can be selected randomly from among the known ones, upon consideration of the intended use of the conductive polymer composition to be produced. Specific examples of typically used conductive materials are carbon black, graphite, carbon powder, carbon fiber, etc.; metals (powder, fiber, etc.) such as silver, copper, nickel, aluminum, and alloys; metal oxides (powder, fiber, etc.) such as stannic oxide, zinc oxide, and titanium oxide; combinations of metal-coated glass beads and glass fiber; metal halides such as cuprous iodide; and mixed conductive materials consisting of metals or metal oxides and other conductive materials. These may be used singly or in combinations of two or more. The amount of these conductive materials to be added is not particularly critical, but suitable amounts are usually 3–1,000 parts by weight, and preferably 5–700 parts by weight, per 100 parts by weight of the aforesaid liquid diene-based polymer.

The present invention is made up in principle of the above-mentioned three ingredients, but other additives can be added, if necessary, without thereby greatly impairing the object of the present invention. For example, multifunctional acrylates such as trifunctional oligoester acrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, hydroxypivalic acid neopentyl glycol diacrylate, and 1,6-hexanediol diacrylate, or unfunctional acrylates such as 2-ethylhexyl acrylate, tetrahydrofurfuryl acrylate, and cyclohexyl acrylate can be added as reactive diluents. In addition, fillers such as mica, vermiculite, calcium carbonate, and slate powder; plasticizers such as dioctyl phthalate as a viscosity modifier; softening agents such as aromatic, naphthenic, and paraffinic oils can be added; or tackifiers such as alkylphenol resins, terpene resins, terphenol resins, xylene formaldehyde resins, rosin, hydrogenated rosin, cumarone resins,

and aliphatic and aromatic petroleum resins can also be added to adjust the stickiness and adhesiveness. Furthermore, antioxidants can be added to enhance weatherability, or silicon compounds can be added as antifoam agents.

The conductive polymer composition of the present invention is produced by combining and mix-kneading the above-mentioned ingredients. Mix-kneading conditions can be determined with consideration of the types, mixing proportions, etc., of the source materials to be used, but the mixture is stirred usually at 0–200°C, and preferably at 10–100°C, for 0.1–1,000 minutes, and preferably for 1–200 minutes. The conductive polymer composition of the present invention thus obtained is liquid, which can then be turned into a conductive elastic cured material when cured at 20–250°C, and preferably at 50–200°C, for 0.1–168 hours, and preferably for 0.5–75 hours.

Effect of the Invention

The conductive polymer composition of the present invention can be produced with great ease, because combining specified materials as source materials eliminates the need for heating to high temperatures at the time of production, the need for mix-kneading under high torque, and the need for special equipment. In other words, a conductive material can be added and dispersed uniformly in the composition by a simple operation involving mixing at temperatures of around room temperature.

Furthermore, the composition of the present invention is liquid, and hence can be cured and formed easily into the desired shape.

Moreover, a conductive elastic cured material that can be obtained by curing the composition of the present invention has excellent conductivity (low volume resistivity).

Accordingly, the conductive polymer composition of the present invention can be used effectively as a pressure-sensitive conductive material, heat generator, conductive coating, conductive adhesive, conductive gasket, electromagnetic shielding material, electric-field relaxation self-fusing tape, coating material, antistatic material, and semiconductive material.

ACTUAL EXAMPLES

Next, the present invention will be illustrated in detail by the use of actual examples.

Actual Examples 1-5

A liquid diene-based polymer, a radical generator, a conductive material, and a reactive diluent (Actual Examples 1, 3, and 4) were mixed in given amounts (parts by weight) at 25°C for 20 minutes as shown in Table 1. The mixture obtained was cured and formed in a press mold under the conditions of a pressure of 100 kgf/cm² and a temperature of 160°C for 1 hour to obtain a 2-mm thick sheet. The tensile strength and volume resistivity were measured on the sheets obtained. The results are shown in Table 1.

Table 1. KEY: (a) Actual Example; (b) composition; (c) liquid diene-based polymer; (d) hydroxyl group-terminated liquid polybutadiene^{*1}; (e) carboxyl group-terminated liquid polybutadiene^{*2}; (f) acryloyl group-terminated liquid polybutadiene^{*3}; (g) radical generator; (h) dicumyl peroxide; (i) benzoyl peroxide; (j) conductive material; (k) metal powder^{*4}; (l) metalcoated fiber^{*5}; (m) reactive diluent; (n) vinyltoluene; (o) trimethylol-propane trimethacrylate; (p) cured product; (q) tensile strength (kgf/cm²)^{*6}; and (r) volume resistivity (Ω-cm).

		(a) 例				
		1	2	3	4	5
(b) 組成	(c) 液体ジエン系ポリマー	20	—	—	—	—
	(d) 水素末端液体ポリブタジエン ^{*1}	—	100	80	—	—
	(e) カルボキシル末端液体ポリブタジエン ^{*2}	—	—	—	80	100
	(f) アクリロイル末端液体ポリブタジエン ^{*3}	—	—	—	—	—
	(g) 重合開始剤	—	—	2	2	2
	(h) 重合開始剤	—	8	—	1	—
(c) 液体ジエン系ポリマー	(i) 重合開始剤	500	—	250	—	250
	(j) 重合開始剤	—	100	50	100	50
	(k) 金属粉末 ^{*4}	30	—	—	10	—
	(l) 金属被覆繊維 ^{*5}	—	—	20	10	—
(d) 硬化物	(m) 反応性希釈剤	50	10	20	10	10
	(n) 重合開始剤	3.0 × 10 ⁻²	6.3 × 10 ⁻¹	1.2 × 10 ⁻¹	8.2 × 10 ⁻²	7.4 × 10 ⁻¹

*1 = Idemitsu Petrochemical (Ltd.); R-45HT; number-average molecular weight = 2,800; OH content = 0.79 mEq/g

*2 = Idemitsu Petrochemical (Ltd.); R-45MA; acid value = 43 mgKOH/g; viscosity = 150 poise/30°C

*3 = Idemitsu Petrochemical (Ltd.); R-45ACR; viscosity = 400 poise/60°C

*4 = Fukuda Kinzoku Hakufun Kogyo (Ltd.); silver-saving conductive composite powder Ni-Ag series; Ag content = 50 weight%; average particle size = 2.45 μm; specific surface area = 250 cm²/g

*5 = Nippon Sheet Glass (Ltd.); aluminum-coated glass fiber "Alumi Coat Fiber"; filament chopped fiber length = 13 [unit illegible]; fiber length = 15 μm

*6 = in accordance with JIS K6301

Comparison Examples 1 and 2

A given amount of natural rubber was masticated, as shown in Table 2. Specifically, the

refining of natural rubber was performed twice at a roll temperature of 55°C and a gap of 0.2 mm, and then a $\frac{3}{4}$ cut was performed alternately for 30 seconds at a gap of 1.4 mm. After said mastication, stearic acid was added to the natural rubber so as to spread to every part; moreover, carbon black was added, first one-half the amount and then the remaining half was added after the $\frac{3}{4}$ cut (roll gap 1.6 mm) was carried out once, followed by another $\frac{3}{4}$ cut (roll gap 1.9 mm). Subsequently, zinc white and sulfur were added to spread to every part, then benzothiazyl disulfide was added, and a $\frac{3}{4}$ cut (roll gap 0.75 mm) was performed three times. A conductive material as shown in Table 2 was added to this, and a $\frac{3}{4}$ cut (roll gap 1.9 mm) was performed three times, followed by 6 repetitions of passing between rolls (roll gap 0.75 mm) and further followed by mix-kneading at a roll gap of 2 mm to obtain a sheet product. The sheet product obtained was placed in a mold of 2 × 150 × 300 mm, and treated at 150°C under applied pressure for 1 hour to obtain a vulcanized sheet. The tensile strength and volume resistivity of the sheets produced were then measured. The results are shown in Table 2.

Table 2. KEY: (a) Comparison Example; (b) rubber mix (parts by weight); (c) natural rubber; (d) zinc white; (e) sulfur; (f) stearic acid; (g) benzothiazyl disulfide; (h) carbon black (channel black); (i) conductive material; (j) metal powder^{*4}; (k) metal-coated fiber^{*5}; (l) properties; (m) tensile strength^{*6} (kgf/cm²); (n) volume resistivity (Ω-cm); (o) others; (p) fiber was crushed during the mastication; and (q) *4~*6: same as in Table 1.

		(c) 比較例	
		1	2
(b) ゴム配合物 (重量部)	(c) 天然ゴム	100	100
	(d) 亜鉛華	5	5
	(e) サルファ	3	3
	(f) ステアリン酸	3	3
	(g) ベンゾチアジルスルファイド	1	1
	(h) カーボンブラック (チャンネルブラック)	50	50
(c) 添物	(i) 金 属 粉 末	500	—
	(j) 金属被覆繊維 ^{*5}	—	100
(l) 性	(m) 引張強度 ^{*6} (kgf/cm ²)	8	14
(n) 質	(o) 体積抵抗率 (Ω-cm)	2.4×10^3	5.8×10^3
(p)	(o) その他	—	(p) 繊維中、繊維が破断された。

(q) *4~*6: 第1表に同じ。